(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 132 455 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
12.09.2001 Bulletin 2001/37

(51) Int Cl.[7]: C10L 1/22, C10L 1/14, C10L 10/00

(21) Application number: 01301299.2

(22) Date of filing: 13.02.2001

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 01.03.2000 US 516289

(71) Applicant: Chevron Oronite Company LLC
San Ramon, CA 94583-4289 (US)

(72) Inventors:
- Ahmadi, Majid R.
Pinole, California 94564 (US)
- Morris, Jack E.
El Cerrito, California 94530 (US)

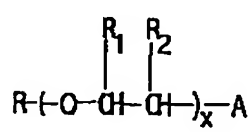
(74) Representative: Nash, David Allan et al
Haseltine Lake & Co.,
Imperial House, 15-19 Kingsway
London WC2B 6UD (GB)

(54) Fuel additive compositions containing mannich condensation products and hydrocarbyl-substituted polyoxyalkylene amines

(57) A novel fuel additive composition comprising:

(a) a Mannich condensation product of (1) a high molecular weight alkyl-substituted hydroxyaromatic compound wherein the alkyl group has a number average molecular weight of from about 300 to about 5,000 (2) an amine which contains an amino group having at least one active hydrogen atom, and (3) an aldehyde, wherein the respective molar ratio of reactants (1), (2) and (3) is 1:0.1-10:0.1-10; and

(b) a hydrocarbyl-substituted polyoxyalkylene amine having the formula:



(I)

or a fuel-soluble salt thereof;

wherein R is a hydrocarbyl group having from about 1 to about 30 carbon atoms;

one of R_1 and R_2 is methyl or ethyl and the other is hydrogen, and each R_1 and R_2 is independently selected in each -O-CHR$_1$-CHR$_2$- unit;

A is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms; and

x is an integer from about 5 to about 100;

and wherein the weight ratio of polyoxyalkylene amine to Mannich condensation product is from about 0.5:1 to about 12:1.

The fuel additive composition of the present invention is useful for the prevention and control of engine oil screen plugging.

EP 1 132 455 A1

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates to fuel additive compositions containing Mannich condensation products and hydrocarbyl-substituted polyoxyalkylene amines. In a further aspect this invention relates to the use of these additive compositions in fuel compositions to prevent and control engine oil screen plugging.

Description of the Related Art

[0002] It is well known that automobile engines end to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports, intake valves, and combustion chambers, due to the oxidation and polymerization of hydrocarbon fuel. Thes deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art.

[0003] For example, polyoxyalkylene amines, or polyether amines, are known to reduce engine deposits when used in fuel compositions. Thus, U.S. Patent No. 5,112,364, issued May 12, 1992 to Rath et al., discloses gasoline-engine fuels which contain from 10 to 2,000 parts per million by weight of a polyetheramine and/or a polyetheramine derivative, wherein the polyetheramine is prepared by reductive amination of a phenol-initiated or alkylphenol-initiated polyether alcohol with ammonia or a primary amine.

[0004] U.S. Patent No. 5,660,601, issued August 26, 1997 to Oppenlander et al., discloses fuels for gasoline engines containing from 10 to 2,000 mg per kg of fuel (i.e., 10 to 2,000 parts per million) of an alkyl-terminated polyetheramine, wherein the alkyl group contains from 2 to 30 carbon atoms and the polyether moiety contains from 12 to 28 butylene oxide units. This patent further teaches that the polyetheramines are prepared by the reaction of an alcohol with butylene oxide, and subsequent amination with ammonia or an amine.

[0005] U.S. Patent No. 4,332,595, issued June 1, 1982 to Herbstman et al., discloses a gasoline detergent additive which is a hydrocarbyl-substituted polyoxypropylene diamine, wherein the hydrocarbyl substituent contains 8 to 18 carbon atoms. This patent further teaches that the additive is prepared by reductive amination of a hydrocarbyl-substituted polyoxypropylene alcohol with ammonia to give a polyoxypropylene amine, which is subsequently reacted with acrylonitrile to give the corresponding *N*-2-cyanoethyl derivative. Hydrogenation in the presence of ammonia then provides the desired hydrocarbyl-substituted polyoxypropylene *N*-3-aminopropyl amine.

[0006] U.S. Patent No. 3,440,029, issued April 22, 1969 to Little et al., discloses a gasoline anti-icing additive which is a hydrocarbyl-substituted polyoxyalkylene amine, wherein the hydrocarbyl substituent contains 8 to 24 carbon atoms. This patent teaches that the additive may be prepared by known processes wherein a hydroxy compound is condensed with an alkylene oxide or mixture of alkylene oxides and then the terminal amino group is attached by either reductive amination or by cyanoethylation followed by hydrogenation. Alternatively, the hydroxy compound or oxyalkylated derivative thereof may be reacted with bis(2-chloroethyl)ether and alkali to make a chlorine-terminated compound, which is then reacted with ammonia to produce the amine-terminated final product.

[0007] U.S. Patent No. 4,247,301, issued January 27, 1981 to Honnen, discloses hydrocarbyl-substituted poly(oxyalkylene) polyamines, wherein the hydrocarbyl group contains from 1 to 30 carbon atoms and the polyamine moiety contains from 2 to. 12 amine nitrogen atoms and from 2 to 40 carbon atoms. This patent teaches that the additives may be prepared by the reaction of a suitable hydrocarbyl-terminated polyether alcohol with a halogenating agent such as HC1, thionyl chloride, or epichlorohydrin to form a polyether chloride, followed by reaction of the polyether chloride with a polyamine to form the desired poly(oxyalkylene) polyamine. This patent also teaches at Example 6 that the polyether chloride may be reacted with ammonia or dimethylamine to form the corresponding polyether amine or polyether dimethylamine.

[0008] U.S. Patent No. 5,752,991 issued May 19, 1998 to Plavac, discloses fuel compositions containing from about 50 to about 2,500 parts per million by weight of a long chain alkylphenyl polyoxyalkylene amine, wherein the alkyl substituent on the phenyl ring has at least 40 carbon atoms.

[0009] Mannich condensation products are also known in the art as fuel additives for the prevention and control of engine deposits. For example, U.S. Patent No. 4, 231,759, issued November 4, 1980 to Udelhofen et al., discloses reaction products obtained by the Mannich condensation of a high molecular weight alkyl-substituted hydroxyaromatic compound, an amine containing an amino group having at least one active hydrogen atom, and an aldehyde, such as formaldehyde. This patent further teaches that such Mannich condensation products are useful detergent additives in

fuels for the control of deposits on carburetor surfaces and intake valves.

[0010] U.S. Patent No. 5,514, 190, issued May 7, 1996 to Cunningham et al., discloses a fuel additive composition for the control of intake valve deposits which comprises (a) the Mannich reaction product of a high molecular weight alkyl-substituted phenol, an amine, and an aldehyde, (b) a poly(oxyalkylene) carbamate, and (c) a poly(oxyalkylene) alcohol, glycol or polyol, or a mono or diether thereof.

[0011] U.S. Parent No. 5,697,988, issued December 16, 1997 to Malfer et al., discloses a fuel additive composition which provides reduced fuel injector, intake valve and combustion chamber deposits which comprises (a) the Mannich reaction product of a high molecular weight alkyl-substituted phenol, an amine, and an aldehyde, (b) a polyoxyalkylene compound, preferably a polyoxyalkylene glycol or monoether derivative thereof, and (c) optionally a poly-alpha-olefin.

[0012] Although hydrocarbyl-substituted polyoxyalkylene amines are generally known to be effective deposit control fuel additives, particularly on engine intake systems and combustion chambers, it has now been found that certain polyoxyalkylene amines may contribute to crankcase sludge and varnish build-up which can ultimately result in engine oil screen plugging and catastrophic engine failure. Accordingly, there exists a need in the art for polyoxyalkylene amine-containing fuel additive compositions which effectively control intake system and combustion chambers deposits, without contributing to the problem of engine oil screen plugging.

SUMMARY OF THE INVENTION

[0013] It has now been discovered that the combination of certain Mannich condensation products with certain hydrocarbyl-substituted polyoxyalkylene amines affords a unique fuel additive composition which provides excellent control of engine oil screen plugging.

[0014] Accordingly, the present invention provides a novel fuel additive composition comprising:

(a) a Mannich condensation product of (1) a high molecular weight alkyl-substituted hydroxyaromatic compound wherein the alkyl group has a number average molecular weight of from about 300 to about 5,000 (2) an amine which contains an amino group having at least one active hydrogen atom, and (3) an aldehyde, wherein the respective molar ratio of reactants (1), (2) and (3) is 1:0.1-10:0.1-10; and

(b) a hydrocarbyl-substituted polyoxyalkylene amine having the formula:

$$R\text{-}(\text{-}O\text{-}\underset{}{\overset{R_1}{\overset{|}{CH}}}\text{-}\overset{R_2}{\overset{|}{CH}}\text{-})_x\text{-}A \qquad (I)$$

or a fuel-soluble salt thereof;

wherein R is a hydrocarbyl group having from about 1 to about 30 carbon atoms;

one of R_1 and R_2 is methyl or ethyl and the other is hydrogen, and each R_1 and R_2 is independently selected in each $\text{-O-CHR}_1\text{-CHR}_2\text{-}$ unit;

A is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms; and

x is an integer from about 5 to about 100;

and wherein the weight ratio of polyoxyalkylene amine to Mannich condensation product is from about 0.5:1 to about 12:1.

[0015] The present invention further provides a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an amount effective to control engine oil screen plugging of a fuel additive composition of the present invention.

[0016] The present invention additionally provides a fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of from about 150°F to 400°F and from about 10 to about 70 weight percent of a fuel additive

composition of the present invention.

[0017] Among other factors, the present invention is based on the surprising discovery that the unique combination of certain Mannich condensation products with certain hydrocarbyl-substituted polyoxyalkylene amines provides excellent control of engine oil screen plugging when employed as additives in fuel compositions.

DETAILED DESCRIPTION OF THE INVENTION

I. The Mannich Condensation Product

[0018] The Mannich reaction products employed in this invention are obtained by condensing an alkyl-substituted hydroxyaromatic compound whose alkyl-substituent has a number average molecular weight of from about 300 to about 5,000 (Mn), preferably polyalkylphenol whose polyalkyl substituent is derived from 1-mono-olefin polymers having a number average molecular weight of from about 300 to about 5,000, more preferably from about 400 to about 3,000; an amine containing at least one >NH group, preferably an alkylene polyamine of the formula

$$H_2N\text{-}(B\text{-}NH\text{-})_mH$$

wherein B is a divalent alkylene radical having 1 to about 10 carbon atoms and m is an integer from 1 to about 10; and an aldehyde, preferably formaldehyde, in the presence of a solvent.

[0019] High molecular weight Mannich reaction products useful as additives in the fuel additive compositions of this invention are preferably prepared according to conventional methods employed for the preparation of Mannich condensation products, using the above-named reactants in the respective molar ratios of high molecular weight alkyl-substituted hydroxyaromatic compound, amine, and aldehyde of approximately 1.0:0.1-10:1-10. A suitable condensation procedure involves adding at a temperature of from room temperature to about 95°C., the formaldehyde reagent (e.g., formalin) to a mixture of amine and alkyl-substituted hydroxyaromatic compounds alone or in an easily removed organic solvent, such as benzene, xylene, or toluene or in solvent-refined neutral oil, and then heating the reaction mixture at an elevated temperature (120°-175°C) while the water of reaction is distilled overhead and separated. The reaction product so obtained is finished by filtration and dilution with solvent as desired.

[0020] Preferred Mannich reaction product additives employed in this invention are derived from high molecular weight Mannich condensation products, formed by reacting an alkylphenol, an ethylene polyamine, and a formaldehyde affording reactants in the respective molar ratio of 1.0:0.5-2.0:1.0-3.0, wherein the alkyl group of the alkylphenol has a number average weight (Mn) of from about 300 to about 5,000. Representative of the high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol and other polyalkylphenols, with polyisobutylphenol being the most preferred. Polyalkylphenols may be obtained by the alkylation, in the presence of an alkylating catalyst such as BF_3, of phenol with high molecular weight polypropylene, polybutylene and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having a number average molecular weight (Mn) of from about 300 to about 5,000.

[0021] The alkyl substituents on the hydroxyaromatic compounds may be derived from high molecular weight polypropylenes, polybutenes, and other polymers of mono-olefins, principally 1-mono-olefins. Also useful are copolymers of mono-olefins with monomers copolymerizable therewith, wherein the copolymer molecule contains at least 90% by weight of mono-olefin units. Specific examples are copolymers of butenes (butene-1, butene-2, and isobutylene) with monomers copolymerizable therewith wherein the copolymer molecule contains at least 90% by weight of propylene and butene units, respectively. Said monomers copolymerizable with propylene or said butenes include monomers containing a small proportion of unreactive polar groups, such as chloro, bromo, keto, ether, or aldehyde, which do not appreciably lower the oil-solubility of the polymer. The comonomers polymerized with propylene or said butenes may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, methylstyrene, p-dimethylstyrene, divinyl benzene and the like. From the foregoing limitation placed on the monomer copolymerized with propylene or said butenes, it is clear that said polymers and copolymers of propylene and said butenes are substantially aliphatic hydrocarbon polymers. Thus, the resulting alkylated phenols contain substantially alkyl hydrocarbon substitutents having a number average molecular weight (Mn) of from about 300 to about 5,000.

[0022] In addition to the foregoing high molecular weight hydroxyaromatic compounds, other phenolic compounds which may be used include, high molecular weight alkyl-substituted derivatives of resorcinol, hydroquinone, cresol, cathechol, xylenol, hydroxy-di-phenyl, benzylphenol, phenethylphenol, naphthol, tolylnaphthol, among others. Preferred for the preparation of such preferred Mannich condensation products are the polyalkylphenol reactants, e.g., polypropylphenol and polybutylphenol, particularly polyisobutylphenol, whose alkyl gmup has a number average molecular weight of about 300 to about 5,000, preferably about 400 to about 3,000, more preferably about 500 to about 2,000, and most preferably about 700 to about 1,500.

[0023] As noted above, the polyalkyl substituent on the polyalkyl hydroxyaromatic compounds employed in the invention may be generally derived from polyolefins which are polymers or copolymers of mono-olefins, particularly 1-mono-olefins, such as ethylene, propylene, butylene, and the like. Preferably, the mono-olefin employed will have 2 to about 24 carbon atoms, and more preferably, about 3 to 12 carbon atoms. More preferred mono-olefins include propylene, butylene, particularly isobutylene, 1-octene and 1-decene. Polyolefins prepared from such mono-olefins include polypropylene, polybutene, especially polyisobutene, and the polyalphaolefins produced from 1-octene and 1-decene.

[0024] The preferred polyisobutenes used to prepare the presently employed polyalkyl hydroxyaromatic compounds are polyisobutenes which comprise at least about 20% of the more reactive methylvinylidene isomer, preferably at least about 50% and more preferably at least about 70% methylvinylidene isomer. Suitable polyisobutenes include those prepared using BF_3 catalysts. The preparation of such polyisobutenes in which the methylvinylidene isomer comprises a high percentage of the total composition is described in U.S. Patent Nos. 4,12,499 and 4,605,808.

[0025] Examples of suitable polyisobutenes having a high alkylvinylidene content include Ultravis 10, a polyisobutene having a molecular weight of about 950 and a methylvinylidine content of about 76%, and Ultravis 30, a polyisobutene having a molecular weight of about 1300 and a methylvinylidene content of about 74%, both available from British Petroleum, and Glissopal 1000, 1300 and 2200, available from BASF.

[0026] The preferred configuration of the alkyl-substituted hydroxyaromatic compound is that of a para-substituted mono-alkylphenol. However, any alkylphenol readily reactive in the Mannich condensation reaction may be employed. Accordingly, ortho mono-alkylphenols and dialkylphenols are suitable for use in this invention.

[0027] Representative amine reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one HN< group suitable for use in the preparation of the Mannich reaction products are well known and include the mono and di-amino alkanes and their substituted analogs, e.g., ethylamine, dimethylamine, dimethylaminopropyl amine, and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolinidine, and piperidine; melamine and their substituted analogs.

[0028] The alkylene polyamine reactants which are useful with this invention include polyamines which are linear, branched, or cyclic; or a mixture of linear, branched and/or cyclic polyamines wherein each alkylene group contains from about 1 to about 10 carbon atoms. A preferred polyamine is a polyamine containing from 2 to 10 nitrogen atoms per molecule or a mixture of polyamines containing an average of from about 2 to about 10 nitrogen atoms per molecule such as ethylenediamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hexaethylene heptamine, heptaethylene octamine, octaethylene nonamine, monaethylene decamine, and mixtures of such amines. Corresponding propylene polyamines such as propylene diamine, dipropylene triamine, tripropylene'tetramine, tetrapropylene pentamine, and pentapropylene hexamine are also suitable reactants. A particularly preferred polyamine is a polyamine or mixture of polyamines having from about 3 to 7 nitrogen atoms, with diethylene triamine or a combination or mixture of ethylene polyamines whose physical and chemical properties approximate that of diethylene triamine being the most preferred. In selecting an appropriate polyamine, consideration should be given to the compatibility of the resulting detergent/dispersant with the gasoline fuel mixture with which it is mixed.

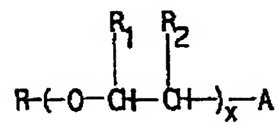
[0029] Ordinarily the most highly preferred polyamine, diethylene triamine, will comprise a commercially available mixture having the general overall physical and/or chemical composition approximating that of diethylene triamine but which can contain minor amounts of branched-chain and cyclic species as well as some linear polyethylene polyamines such as triethylene tetramine and tetraethylene pentamine. For best results, such mixtures should contain at least 50% and preferably at least 70% by weight of the linear polyethylene polyamines enriched in diethylene triamine.

[0030] The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus, the alkylene polyamines are obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloro alkanes having 2 to 6 carbon atoms and the chlorines on different carbons.

[0031] Representative aldehydes for use in the preparation of the high molecular weight Mannich reaction products employed in this invention include the aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, and stearaldehyde. Aromatic aldehydes which may be used include benzaldehyde and salicylaldehyde. Illustrative heterocyclic aldehydes for use herein are furfural and thiophene aldehyde, etc. Also useful are formaldehyde-producing reagents such as paraformaldehyde, or aqueous formaldehyde solutions such as formalin. Most preferred is formaldehyde or formalin.

II. The Hydrocarbyl-Susbstituted Polyoxyalkylene Amine

[0032] The hydrocarbyl-substituted polyoxyalkylene amines employed in the present invention have the general formula:



(I)

wherein R, R_1, R_2, A, and x are as defined above.

[0033] In Formula I, above, R is a hydrocarbyl group having from about 1 to about 30 carbon atoms. Preferably, R is an alkyl or alkylphenyl group. More preferably, R is an alkylphenyl group, wherein the alkyl moiety is a straight or branched chain alkyl of from about 1 to about 24 carbon atoms.

[0034] Also in Formula I above, one of R_1 and R_2 is methyl or ethyl, and the other is hydrogen. In other words, the oxyalkylene units may be oxypropylene or oxybutylene. Mixtures of oxypropylene and oxybutylene units are also contemplated for use in this invention. Preferably one of R_1 and R_2 is methyl, and the other is hydrogen. That is, the preferred oxyalkylene unit is oxypropylene.

[0035] In general, A is amino, N-alkyl amino having from about 1 to about 20 carbon atoms in the alkyl group, preferably about 1 to about 6 carbon atoms, more preferably about 1 to about 4 carbon atoms; N,N-dialkyl amino having from about 1 to about 20 carbon atoms in each alkyl group, preferably about 1 to about 6 carbon atoms, more preferably about 1 to about 4 carbon atoms; or a polyamine moiety having from about 2 to about 12 amine nitrogen atoms and from about 2 to about 40 carbon atoms, preferably about 2 to 12 amine nitrogen atoms and about 2 to 24 carbon atoms. More preferably, A is amino or a polyamine moiety derived from a polyalkylene polyamine, including alkylene diamine. Most preferably, A is amino or a polyamine moiety derived from ethylene diamine or diethylene triamine.

[0036] Preferably, x is an integer from about 5 to about 50, more preferably from about 8 to about 30, and most preferably from about 10 to about 25.

[0037] The compounds employed in the present invention will generally have a sufficient molecular weight so as to be non-volatile at normal engine intake valve operating temperatures (about 200°-250°C.). Typically, the molecular weight of the polyoxyalkylene amine compounds employed in this invention will range from about 600 to about 10,000.

[0038] Fuel-soluble salts of the compounds of formula I can be readily prepared for those compounds containing an amino or substituted amino group and such salts are contemplated to be useful for preventing or controlling engine deposits. Suitable salts include, for example, those obtained by protonating the amino moiety with a strong organic acid, such as an alkyl- or arylsulfonic acid. Preferred salts are derived from toluenesulfonic acid and methanesulfonic acid.

Definitions

[0039] As used herein, the following terms have the following meanings unless expressly stated to the contrary.

[0040] The term "amino" refers to the group: $-NH_2$.

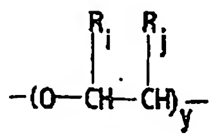
[0041] The term "*N*-alkylamino" refers to the group: $-NHR_a$ wherein R_a is an alkyl group. The term "*N,N*-dialkylamino" refers to the group: $—NR_bR_c$, wherein R_b and R_c are alkyl groups.

[0042] The term "hydrocarbyl" refers to an organic radical primarily composed of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., aralkyl or alkaryl. Such hydrocarbyl groups are generally free of aliphatic unsaturation, i.e., olefinic or acetylenic unsaturation, but may contain minor amounts of heteroatoms, such as oxygen or nitrogen, or halogens, such as chlorine. The term "alkyl" refers to both straight- and branched-chain alkyl groups.

[0043] The term "lower alkyl" refers to alkyl groups having 1 to about 6 carbon atoms and includes primary, secondary, and tertiary alkyl groups. Typical lower alkyl groups include, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, n-hexyl, and the like.

[0044] The term "alkylene" refers to straight- and branched-chain alkylene groups having at least 2 carbon atoms. Typical alkylene groups include, for example, ethylene ($-CH_2CH_2-$), propylene ($-CH_2CH_2CH_2-$), isopropylene ($-CH(CH_3)CH_2-$), n-butylene ($-CH_2CH_2CH_2CH_2-$), sec-butylene ($-CH(CH_2CH_3)CH_2-$), n-pentylene ($-CH_2CH_2CH_2CH_2CH_2-$), and the like.

[0045] The term "polyoxyalkylene" refers to a polymer or oligomer having the general formula:



wherein R_i and R_j are each independently hydrogen or lower alkyl groups, and y is an integer from about 5 to about 100. When referring herein to the number of oxyalkylene units in a particular polyoxyalkylene compound, it is to be understood that this number refers to the average number of oxyalkylene units in such compounds unless expressly stated to the contrary.

General Synthetic Procedures

[0046] The hydrocarbyl-substituted polyoxyalkylene amines employed in this invention may be prepared by the following general methods and procedures. It should be appreciated that where typical or preferred process conditions (e.g., reaction temperatures, times, mole ratios of reactants, solvents, pressures, etc.) are given, other process conditions may also be used unless otherwise stated. Optimum reaction conditions may vary with the particular reactants or solvents used, but such conditions can be determined by one skilled in the art by routine optimization procedures.

[0047] The hydrocarbyl-substituted polyoxyalkylene amines employed in the present invention contain (a) a hydrocarbyl-substituted polyoxyalkylene component, and (b) an amine component.

A. The Hydrocarbyl-Substituted Polyoxyalkylene Component

[0048] The hydrocarbyl-substituted polyoxyalkylene polymers which are utilized in preparing the hydrocarbyl-substituted polyoxyalkylene amines employed in the present invention are monohydroxy compounds, i.e., alcohols, often termed hydrocarbyl "capped" polyoxyalkylene glycols and are to be distinguished from the polyoxyalkylene glycols (diols), which are not hydrocarbyl terminated, i.e., not capped. The hydrocarbyl-substituted polyoxyalkylene alcohols are produced by the addition of lower alkylene oxides, such as propylene oxide, or the butylene oxides, to the hydroxy compound, ROH, under polymerization conditions, wherein R is the hydrocarbyl group, as defined above, which caps the polyoxyalkylene chain. Preferred polyoxyalkylene polymers are those derived from C_3 to C_4 oxyalkylene units. Methods of production and properties of these polymers are disclosed in U.S. Patent Nos. 2,841,479 and 2,782,240 and Kirk-Othmer's *"Encyclopedia of Chemical Technology"*, Volume 19, page 507. In the polymerization reaction, a single type of alkylene oxide may be employed, e.g., propylene oxide, in which case the product is a homopolymer, e.g., a polyoxypropylene alcohol. However, copolymers are equally satisfactory and random copolymers are readily prepared by contacting the hydroxy-containing compound with a mixture of alkylene oxides, such as a mixture of propylene and butylene oxides. Block copolymers of oxyalkylene units also provide satisfactory polyoxyalkylene units for the practice of the present invention.

[0049] The amount of alkylene oxide employed in this reaction will generally depend on the number of oxyalkylene units desired in the product. Typically, the molar ratio of alkylene oxide to hydroxy-containing compound will range from about 5:1 to about 100:1; preferably, from about 5:1 to about 50:1, more preferably from about 8:1 to about 30:1.

[0050] Alkylene oxides suitable for use in this polymerization reaction include propylene oxide and butylene oxides, such as 1,2-butylene oxide (1,2-epoxybutane) and 2,3-butylene oxide (2,3-epoxybutane). Preferred alkylene oxides are propylene oxide and 1,2-butylene oxide, both individually and in mixtures thereof.

[0051] The hydrocarbyl moiety, R, which terminates the polyoxyalkylene chain will generally contain from about 1 to about 30 carbon atoms, preferably from about 2 to about 20 carbon atoms, and more preferably from about 4 to about 18 carbon atoms, and is generally derived from the monohydroxy compound, ROH, which is the initial site of the alkylene oxide addition in the polymerization reaction. Such monohydroxy compounds are preferably aliphatic or aromatic alcohols having from about 1 to about 30 carbon atoms, more preferably and alkanol or an alkylphenol, and most preferably an alkyphenol wherein the alkyl substituent is a straight or branched chain alkyl of from about 1 to about 24 carbon atoms. Preferred alkylphenols include those wherein the alkyl substituent contains from about 4 to about 16 carbon atoms. An especially preferred alkylphenol is one wherein the alkyl group is obtained by polymerizing propylene to an average of 4 propylene units, that is, about 12 carbon atoms, having the common name of propylene tetramer. The resulting alkylphenol is commonly called tetrapropenylphenol or, more generically, dodecylphenol. Preferred alkylphenol-initiated polyoxyalkylene compounds may be termed either alkylphenylpolyoxyalkylene alcohols or polyalkoxylated alkylphenols.

B. The Amine Component

[0052] As indicated above, the hydrocarbyl-substituted polyoxyalkylene amines employed in the present invention contain an amine component.

[0053] In general, the amine component will contain an average of at least about one basic nitrogen atom per molecule. A "basic nitrogen atom" is one that is titratable by a strong acid, for example, a primary, secondary, or tertiary amine nitrogen; as distinguished from, for example, an carbamyl nitrogen, e.g., -OC(O)NH-, which is not titratable with a strong acid. Preferably, at least one of the basic nitrogen atoms of the amine component will be primary or secondary amine nitrogen, more preferably at least one will be a primary amine nitrogen.

[0054] The amine component of the hydrocarbyl-substituted polyoxyalkylene amines employed in this invention is preferably derived from ammonia, a primary alkyl or secondary dialkyl monoamine, or a polyamine having a terminal amino nitrogen atom.

[0055] Primary alkyl monoamines useful in preparing compounds of the present invention contain 1 nitrogen atom and from about 1 to about 20 carbon atoms, more preferably about 1 to 6 carbon atoms, most preferably 1 to 4 carbon atoms. Examples of suitable monoamines include *N*-methylamine, *N*-ethylamine, *N*-n-propylamine, *N*-isopropylamine, *N*-n-butylamine, *N*-isobutylamine, *N*-sec-butylamine, *N*-tert-butylamine, *N*-n-pentylamine, N-cyclopentylamine, N-n-hexylamine, N-cyclohexylamine, N-octylamine, N-decylamine, N-dodecylamine, N-octadecylamine, N-benzylamine, N-(2-phenylethyl)amine, 2-aminoethanol, 3-amino-1-propanol, 2-(2-aminoethoxy)ethanol, N-(2-methoxyethyl)amine, N-(2-ethoxyethyl)amine and the like. Preferred primary amines are N-methylamine, N-ethylamine and N-n-propylamine.

[0056] The amine component of the presently employed fuel additive may also be derived from a secondary dialkyl monoamine. The alkyl groups of the secondary amine may be the same or different and will generally each contain about 1 to about 20 carbon atoms, more preferably about 1 to about 6 carbon atoms, most preferably about 1 to about 4 carbon atoms. One or both of the alkyl groups may also contain one or more oxygen atoms.

[0057] Preferably, the alkyl groups of the secondary amine are independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, 2-hydroxyethyl and 2-methoxyethyl. More preferably, the alkyl groups are methyl, ethyl or propyl.

[0058] Typical secondary amines which may be used in this invention include N,N-dimethylamine, N,N-diethylamine, N,N-di-n-propylamine, N,N-diisopropylamine, N,N-di-n-butylamine, N,N-di-sec-butylamine, N,N-di-n-pentylamine, N, N-di-n-hexylamine, N,N-dicyclohexylamine, N,N-dioctylamine, N-cthyl-N-methylamine, N-methyl-N-n-propylamine, N-n-butyl-N-methylamine, N-methyl-N-octylamine, N-ethyl-N-isopropylamine, N-ethyl-N-octylamine, N,N-di(2-hydroxyethyl)amine, N,N-di(3-hydroxypropyl)amine, N,N-di(ethoxyethyl)amine, N,N-di(propoxyethyl)amine and the like. Preferred secondary amines are N,N-dimethylamine, N,N-diethylamine and N,N-di-n-propylamine.

[0059] Cyclic secondary amines may also be used to form the additives employed in this invention. In such cyclic compounds, the alkyl groups, when taken together, form one or more 5- or 6-membered rings containing up to about 20 carbon atoms. The ring containing the amine nitrogen atom is generally saturated, but may be fused to one or more saturated or unsaturated rings. The rings may be substituted with hydrocarbyl groups of from 1 to about 10 carbon atoms and may contain one or more oxygen atoms.

[0060] Suitable cyclic secondary amines include piperidine, 4-methylpiperidine, pyrrolidine, morpholine, 2,6-dimethylmorpholine and the like.

[0061] Suitable polyamines can have a straight- or branched-chain structure and maybe cyclic or acyclic or combinations thereof. Generally, the amine nitrogen atoms of such polyamines will be separated from one another by at least two carbon atoms, i.e., polyamines having an aminal structure are not suitable. The polyamine may also contain one or more oxygen atoms, typically present as an ether or a hydroxyl group. Polyamines having a carbon-to-nitrogen ratio of from about 1:1 to about 10:1 are particularly preferred.

[0062] In preparing the polyoxyalkylene amine compounds employed in this invention using a polyamine where the various nitrogen atoms of the polyamine are not geometrically equivalent, several substitutional isomers are possible and each of these possible isomers is encompassed within this invention.

[0063] A particularly preferred group of polyamines for use in the present invention are polyalkylene polyamines, including alkylene diamines. Such polyalkylene polyamines will typically contain from about 2 to about 12 nitrogen atoms and from about 2 to about 40 carbon atoms, preferably about 2 to 24 carbon atoms. Preferably, the alkylene groups of such polyalkylene polyamines will contain from about 2 to about 6 carbon atoms, more preferably from about 2 to about 4 carbon atoms.

[0064] Examples of suitable polyalkylene polyamines include ethylenediamine, propylenediamine, isopropylenediamine, butylenediamine, pentylenediamine, hexylenediamine, diethylenetriamine, dipropylenetriamine, dimethylaminopropylamine, diisopropylenetriamine, dibutylenetriamine, di-sec-butylenetriamine, triethylenetetraamine, tripropylenetetraamine, triisobutylenetetraamine, tetraethylenepentamine, pentaethylenehexamine, dimethylaminopropylamine, and mixtures thereof.

[0065] Particularly suitable polyalkylene polyamines are those having the formula:

$$H_2N\text{-}(R_3\text{-}NH)_z\text{-}H$$

wherein R_3 is a straight- or branched-chain alkylene group having from about 2 to about 6 carbon atoms, preferably from about 2 to about 4 carbon atoms, most preferably about 2 carbon atoms, i.e., ethylene ($-CH_2CH_2-$); and z is an integer from about 1 to about 4, preferably about 1 or about 2.

[0066] Particularly preferred polyalkylene polyamines are ethylenediamine, diethylenetriamine, triethylenetetraamine, and tetraethylenepentamine. Most preferred are ethylenediamine and diethylenetriamine, especially ethylenediamine.

[0067] Also contemplated for use in the present invention are cyclic polyamines having one or more 5- to 6-membered rings. Such cyclic polyamines compounds include piperazine, 2-methylpiperazine, N-(2-aminoethyl)piperazine, N-(2-hydroxyethyl)piperazine, 1,2-bis-(N-piperazinyl)ethane, 3-aminopyrrolidine, N-(2-aminoethyl)pyrrolidine, and the like. Among the cyclic polyamines, the piperazines are preferred.

[0068] Many of the polyamines suitable for use in the present invention are commercially available and others may be prepared by methods which are well known in the art. For example, methods for preparing amines and their reactions are detailed in Sidgewick's *"The Organic Chemistry of Nitrogen"*, Clarendon Press, Oxford, 1966; Noller's *"Chemistry of Organic Compounds"*, Saunders, Philadelphia, 2nd Ed., 1957; and Kirk-Othmer's *"Encyclopedia of Chemical Technology"*, 2nd Ed., especially Volume 2, pp. 99-116.

C. Preparation of the Hydrocarbyl-Substituted Polyoxyalkylene Amine

[0069] The polyoxyalkylene amine additives employed in this invention may be conveniently prepared by reacting a hydrocarbyl-substituted polyoxyalkylene alcohol, either directly or through an intermediate, with a nitrogen-containing compound, such as ammonia, a primary or secondary alkyl monoamine or a polyamine, as described herein.

[0070] The hydrocarbyl-substituted polyoxyalkylene alcohols used to form the polyoxyalkylene amines employed in the present invention are typically known compounds that can be prepared using conventional procedures. Suitable procedures for preparing such compounds are taught, for example, in U.S. Patent Nos. 2,782,240 and 2,841,479, as well as U.S. Patent No. 4,881,945, the disclosures of which are incorporated herein by reference.

[0071] Preferably, the polyoxyalkylene alcohols are prepared by contacting an alkoxide or phenoxide metal salt with from about 5 to about 100 molar equivalents of an alkylene oxide, such as propylene oxide or butylene oxide, or mixtures of alkylene oxides.

[0072] Typically, the alkoxide or phenoxide metal salt is prepared by contacting the corresponding hydroxy compound with a strong base, such as sodium hydride, potassium hydride, sodium amide, and the like, in an inert solvent, such as toluene, xylene, and the like, under substantially anhydrous conditions at a temperature in the range from about -10°C to about 120°C for from about 0.25 to about 3 hours.

[0073] The alkoxide or phenoxide metal salt is generally not isolated, but is reacted *in situ* with the alkylene oxide or mixture of alkylene oxides to provide, after neutralization, the polyoxyalkylene alcohol. This polymerization reaction is typically conducted in a substantially anhydrous inert solvent at a temperature of from about 30°C to about 150°C for from about 2 to about 120 hours. Suitable solvents for this reaction, include toluene, xylene, and the like. Typically, the reaction is conducted at a pressure sufficient to contain the reactants and the solvent, preferably at atmospheric or ambient pressure.

[0074] The hydrocarbyl-substituted polyoxyalkylene alcohol may then be converted to the desired polyoxyalkylene amine by a variety of procedures known in the art.

[0075] For example, the terminal hydroxy group on the hydrocarbyl-substituted polyoxyalkylene alcohol may first be converted to a suitable leaving group, such as a mesylate, chloride or bromide, and the like, by reaction with a suitable reagent, such as methanesulfonyl chloride. The resulting polyoxyalkylene mesylate or equivalent intermediate may then be converted to a phthalimide derivative by reaction with potassium phthalimide in the presence of a suitable solvent, such as *N,N*-dimethylformamide. The polyoxyalkylene phthalimide derivative is subsequently converted to the desired hydrocarbyl-substituted polyoxyalkylene amine by reaction with a suitable amine, such as hydrazine.

[0076] The polyoxyalkylene alcohol may also be converted to the corresponding polyoxyalkylene chloride by reaction with a suitable halogenating agent, such as HC1, thionyl chloride, or epichlorohydrin, followed by displacement of the chloride with a suitable amine, such as ammonia, a primary or secondary alkyl monoamine, or a polyamine, as described, for example, in U.S. Patent No. 4,247,301 to Honnen, the disclosure of which is incorporated herein by reference.

[0077] Alternatively, the hydrocarbyl-substituted polyoxyalkylene amines employed in the present invention may be prepared from the corresponding polyoxyalkylene alcohol by a process commonly referred to as reductive amination,

such as described in U.S. Patent No. 5,112,364 to Rath et al. and U.S. Patent No. 4,332,595 to Herbstman et al., the disclosures of which are incorporated herein by reference.

[0078] In the reductive amination procedure, the hydrocarbyl-substituted polyoxyalkylene alcohol is aminated with an appropriate amine, such as ammonia or a primary alkyl monoamine, in the presence of hydrogen and a hydrogenation-dehydrogenation catalyst. The amination reaction is typically carried out at temperatures in the range of about 160°C to about 250°C and pressures of about 1,000 to about 5.000 psig, preferably about 1,500 to about 3,000 psig. Suitable hydrogenatlion-dehydrogenation catalysts include those containing platinum, palladium, cobalt, nickel, copper, or chromium, or mixtures thereof. Generally, an excess of the ammonia or amine reactant is used, such as about a 5-fold to about 60-fold molar excess, and preferably about a 10-fold to about 40-fold molar excess, of ammonia or amine.

[0079] When the reductive amination is carried out with a polyamine reactant, tine amination is preferably conducted using a two-step procedure as described in European Patent Application Publication No. EP 0,781,793, published July 2. 1997, the disclosure of which is incorporated herein by reference in its entirety. According to this procedure, a polyoxyalkylene alcohol is first contacted with a hydrogenation-dehydrogenation catalyst at a temperature of at least 230°C to provide a polymeric carbonyl intermediate, which is subsequently reacted with a polyamine at a temperature below about 190°C in the presence of hydrogen and a hydrogenation catalyst to produce the polyoxyalkylene polyamine adduct.

[0080] The hydrocarbyl-substituted polyoxyalkylene amines obtained by amination can be added as such to hydrocarbon fuels.

Fuel Compositions

[0081] The fuel additive composition of the present invention will generally be employed in hydrocarbon fuels to prevent and control engine oil screen plugging. Typically, the desired control of oil screen plugging will be achieved by operating an internal combustion engine with a fuel composition containing the additive composition of the present invention. The proper concentration of additive necessary to achieve the desired control of oil screen plugging varies depending upon the type of fuel employed, the type of engine, engine oil, operating conditions and the presence of other fuel additives.

[0082] Generally, the present fuel additive composition will be employed in a hydrocarbon fuel in a concentration ranging from about 20 to about 4,000 parts per million (ppm) by weight, preferably from about 20 to about 2,500 ppm.

[0083] In terms of individual components, hydrocarbon fuel containing the fuel additive composition of this invention will generally contain about 10 to about 2,000 ppm, preferably about 10 to about 500 ppm, of the Mannich condensation product component and about 10 to about 2,000 ppm, preferably about 10 to about 1,000 ppm, of the polyoxyalkylene amine component. The weight ratio of the polyoxyalkylene amine to Mannich condensation product will generally range from about 0.5:1 to about 12:1, and will preferably be about 0.5:1 to about 5:1.

[0084] The fuel additive composition of the present invention may be formulated as a concentrate using an inert stable oleophilic (i.e., dissolves in gasoline) organic solvent boiling in the range of about 150°F. to 400°F. (about 65°C. to 205°C.). Preferably, an aliphatic or an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols containing about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol and the like, in combination with hydrocarbon solvents are also suitable for use with the present additives. In the concentrate, the amount of the additive will generally range from about 10 to about 70 weight percent, preferably 10 to 50 weight percent, more preferably from 20 to 40 weight percent.

[0085] In gasoline fuels, other fuel additives may be employed with the additive composition of the present invention, including, for example, oxygenates, such as t-butyl methyl ether, antiknock agents, such as methylcyclopentadienyl manganese tricarbonyl, and other dispersants/detergents, such as hydrocarbyl amines, or succinimides. Additionally, antioxidants, metal deactivators, demulsifiers and carburetor or fuel injector detergents may be present.

[0086] In diesel fuels, other well-known additives can be employed, such as pour point depressants, flow improvers, cetane improvers, and the like.

[0087] A fuel-soluble, nonvolatile carrier fluid or oil may also be used with the fuel additive composition of this invention. The carrier fluid is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the nonvolatile residue (NVR), or solvent-free liquid fraction of the fuel additive composition while not overwhelmingly contributing to octane requirement increase. The carrier fluid may be a natural or synthetic fluid, such as mineral oil, refined petroleum oils, synthetic polyalkanes and alkenes, including hydrogenated and unhydrogenated polyalphaolefins, and synthetic polyoxyalkylene-derived fluids, such as those described, for example, in U.S. Patent No. 4,191,537 to Lewis, and polyesters, such as those described, for example, in U.S. Patent Nos. 3,756,793 to Robinson and 5,004,478 to Vogel et al., and in European Patent Application Nos. 356,726, published March 7, 1990, and 382,159, published August 16, 1990.

[0088] These carrier fluids are believed to act as a carrier for the fuel additive composition of the present invention and to assist in the control of oil screen plugging, as well as engine intake system deposits. The carrier fluid may also

exhibit synergistic oil screen plugging control properties when used in combination with the fuel additive composition of this invention.

[0089] The carrier fluids are typically employed in amounts ranging from about 25 to about 5000 ppm by weight of the hydrocarbon fuel, preferably from 100 to 3000 ppm of the fuel. Preferably, the ratio of carrier fluid to fuel additive will range from about 0.2:1 to about 10:1, more preferably from 0.5:1 to 3:1.

[0090] When employed in a fuel concentrate, carrier fluids will generally be present in amounts ranging from about 20 to about 60 weight percent, preferably from 30 to 50 weight percent.

EXAMPLES

[0091] The following examples are presented to illustrate specific embodiments of the present invention and synthetic preparations thereof and should not be interpreted as limitations upon the scope of the invention.

Example 1

Preparation of Dodecylphenoxy Poly(oxypropylene) Amine

[0092] A dodecylphenoxypoly(oxypropylene) amine was prepared by the reductive amination with ammonia a dodecylphenoxy poly(oxypropylene) alcohol having an average molecular weight of about 1000. The dodecylphenoxypoly (oxypropylene) alcohol was prepared from dodecylphenol and propylene oxide, in accordance with the procedures described in U.S. Patent Nos. 4,191,537; 2,782,240 and 2,841,479, as well as in Kirk-Othmer, "Encyclopedia of Chemical Technology", 4th edition, Volume 19, 1996, page 722. The reductive amination of the dodecylphenoxypoly(oxypropylene) alcohol was carried out using conventional techniques as described in U.S. Patent Nos. 5,112,364; 4,609,377 and 3,440,029.

Example 2

Preparation of Dodecylphenoxy Poly(oxypropylene) Amine

[0093] A dodecylphenoxypoly(oxypropylene) amine was prepared by the reductive animation with ammonia a dodecylphenoxy poly(oxypropylene) alcohol having an average molecular weight of about 1400. The dodecylphenoxypoly (oxypropylene) alcohol was prepared from dodecylphenol and propylene oxide, in accordance with the procedures described in U.S. Patent Nos. 4,191,537; 2,782,240 and 2,841,479, as well as in Kirk-Othmer, "Encyclopedia of Chemical Technology", 4th edition, Volume 19, 1996, page 722. The reductive amination of the dodecylphenoxypoly(oxypropylene) alcohol was carried out using conventional techniques as described in U.S. Patent Nos. 5,112,364; 4,609,377 and 3,440,029.

Example 3

Preparation of Dodecylphenoxy Poly(oxybutylene) Amine

[0094] A dodecylphenoxypoly(oxybutylene) amine was prepared by the reductive amination with ammonia of a dodecylphenoxy poly(oxybutylene) alcohol having an average molecular weight of about 1600. The dodecylphenoxy poly (oxybutylene) alcohol was prepared from dodecylphenol and butylene oxide, in accordance with the procedures described in U.S. Patent Nos. 4,191,537; 2,782,240 and 2,841,479, as well as in Kirk-Othmer, "Encyclopedia of Chemical Technology", 4th edition, Volume 19, 1996, page 722. The reductive amination of the dodecylphenoxy poly(oxybutylene) alcohol was carried out using conventional techniques as described in U.S. Patent Nos. 5,112,364; 4,609,377 and 3,440,029.

Example 4

Preparation of Dodecylphenoxy Poly(oxybutylene)poly(oxypropylene) Amine

[0095] A dodecylphenoxypoly(oxybutylene)poly(oxypropylene) amine was prepared by the reductive amination with ammonia of the random copolymer poly(oxyalkylene) alcohol, dodecylphenoxy poly(oxybutylene)poly(oxypropylene) alcohol, wherein the alcohol has an average molecular weight of about 1598. The poly(oxyalkylene) alcohol was prepared from dodecylphenol using a 75/25 weight/weight ratio of butylene oxide and propylene oxide, in accordance with the procedures described in U.S. Patent Nos. 4,191,537; 2,782,240 and 2,841,479, as well as in Kirk-Othmer, "Ency-

clopedia of Chemical Technology", 4th edition, Volume 19, 1996, page 722. The reductive amination of the poly(oxyalkylene) alcohol was carried out using conventional techniques as described in U.S. Patent Nos. 5,112,364; 4,609,377 and 3,440,029.

Example 5

Preparation of Mannich Condensation Product

[0096] Phenol was combined with Glissopal 1000 polyisobutylene (about 950 molecular weight, available from BASF) containing at least 70% material with methylvinylidene end groups, in the presence of a BF_3-phenol catalyst, to produce a polyisobutylphenol that was essentially all mono-substituted in the para-position. After BF_3 neutralization and removal and dilution with Exxon Aromatic 100 solvent, the diluted polyisobutylphenol had a hydroxyl number of 40.3 mg KOH/g and a nonvolatile residue content of 76.4%. The alkylation process, while the nonvolatile residue contained 7% unconverted polyisobutylene. 3232 g of the aforementioned diluted polyisobutylphenol were charged to a 5-L glass reaction vessel equipped with an agitator, heating mantle, overhead condenser, and Dean-Stark trap. With the reactor temperature at ambient (23°C), 240.6 g of diethylenetriamine (Baker Chemical Company, 99.38% assay) was charged to the reactor and mixed to uniformity with the diluted polyisobutylphenol. The reactor was then heated to 80°C over 30 minutes in preparation for formalin charging.

[0097] The formalin was from Baker Chemical Company and contained 37.3% formaldehyde, 12% methanol, and 50.7% water. The formalin was charged over 150 minutes while continuing to heat to 91-93°C. The temperature reached a maximum of 99°C during this heating period due to the exothermic reaction with the formaldehyde. A temperature of 91-92°C was held for 60 minutes to complete the initial reaction.

[0098] The reaction mixture was then heated to 150°C over 81 minutes and at the same time the pressure was reduced to 240 mm Hg. Much of the water of reaction and some solvent were distilled overhead and separated during the heating. Except for the solvent hold-up in the Dean-Stark trap, the rest of the distilled solvent was continuously returned to the reactor. The final conditions of 144-151°C and 233-243 mm Hg were held for 136 minutes to complete the reaction and removal of water.

[0099] The reaction yield was 3508 g of crude Mannich. After cooling the reactor contents to 85°C, a sample of the crude Mannich gave a nonvolatile residue analysis of 82.0%. The crude Mannich was then diluted with 1940 g of Exxon Aromatic 100 solvent. It was then filtered using 36 g of Celite HyFlo Super Cel diatomaceous earth as body feed and 16 g as a filter precoat. The yield of bright and clear filtrate was 5265 g.

The nonvolatile residue content of the filtered product was 51.9% and the nitrogen content was 1.74%. The actives content was 50% based on the assumption that the unconverted polyisobutylene in the nonvolatile residue is not an active dispersant.

Example 6

Multi-Cylinder Crankcase Harm Screening Test

[0100] The fuel additive composition of the present invention was tested in a laboratory multi-cylinder engine to evaluate its performance in controlling oil screen plugging.

[0101] A 1994 Ford 2.3 liter single overhead cam, in-line four cylinder engine was used. The major engine dimensions set forth in Table I. Each test was carried out for 80 hours (24 hours per day) on a prescribed test cycle, at the end of which the engine was disassembled and the crankcase oil pick-up tube and screen assembly was removed. The cycle for engine operation during the test is set forth in Table II. The oil pick-up tube inlet screen was then evaluated using methodology described in Coordinating Research Council Manual 12 (Sludge Rating Manual, CRC manual 12) to determine the percentage of area clogged. A clean oil screen (free of sludge or debris) indicates favorable crankcase performance. An oil screen with significant clogging indicates poor crankcase performance.

[0102] As part of the Crankcase Harm Screening Test procedure, the engine was physically modified to increase the tendency for sludge and varnish formation. The physical modifications are set forth in Table III. Also specified as part of the test procedure, the crankcase lubricating oil used for all test runs was Chevron 500N oil containing a commercial wear inhibitor. No detergent or dispersant additives were added to the lubricating oil. All test runs were made with the same base gasoline, which was manufactured by Phillips Petroleum Company and is known as Phillips "J" Reference gasoline. The basic properties of the base gasoline are set forth in Table IV.

Table I

Engine Dimensions	
Bore	9.60 cm
Stroke	7.94 cm
Displacement Volume	2.30 liter
Compression Ratio	9.50:1

Table II

Test Cycle - 3 Stage Test, 80 hours total			
(20 loops @ 240 minutes per loop)	Stage 1	Stage 2	Stage 3
Duration per loop, min.	120	75	45
Speed, rpm	2500	2500	800
Loading, bhp	33	33	--
Coolant Temp., deg.F	125	185	115
Oil Temp., deg.F	155	210	115
Intake Air Temp., deg.F	90	90	90

Table III

Engine Physical Modifications
0.080 inch ring gaps
Finned Rocker Cover
Addition of Camshaft Baffle Plate
Addition of Blow-by Oil Separator

Table IV

Fuel Specifications	
Phillips "J" Reference Fuel	
API Gravity	54.2 @ 60 deg.F
Specific Gravity	0.762 @ 60 deg.F
Sulfur	0.0114 wt.%
T10	127 deg.F
T50	219 deg.F
T90	328 deg.F
Aromatics	42.0 vol.%
Olefins	15.3 vol.%
Paraffins+Naphthenes	42.7 vol.%

[0103] The test compounds were admixed with the base fuel to give the concentrations indicated in Table V. The percentage of oil screen plugging is also reported in Table V for each of the test samples.

Table V

Ford 2.3 Liter Crankcase Harm Test

Sample	Concentration, ppma[8]	Percent Oil Screen Plugging
Polyoxypropylene Amine[1]	200	100
Polyoxypropylene Amine[2]	200	100
Polyoxypropylene Amine[3]	200	95
Polyoxypropylene Amine/Mannich Product[4]	150/50	1
Polyoxypropylene Amine/Mannich Product[5]	150/50	1
Polyoxybutylene Amine[6]	200	28[9]
Polyoxybutylene Amine/Mannich Product[7]	150/50	5

[1] Dodecylphenoxypolyoxypropylene amine prepared as described in Example 1.

[2] Dodecylphenoxypolyoxypropylene amine prepared as described in Example 1.

[3] Dodecylphenoxypolyoxypropylene amine prepared as described in Example 2.

[4] Mixture of 150 ppma dodecylphenoxypolyoxypropylene amine prepared as described in Example 1 and 50 ppma of the Mannich condensation product prepared as described in Example 5.

[5] Mixture of 150 ppma dodecylphenoxypolyoxypropylene amine prepared as described in Example 2 and 50 ppma of the Mannich condensation product prepared as described in Example 5.

[6] Dodecylphenoxypolyoxybutylene amine prepared as described in Example 3.

[7] Mixture of 150 ppma dodecylphenoxypolyoxybutylene amine prepared as described in Example 3 and 50 ppma of the Mannich condensation product prepared as described in Example 5.

[8] Parts per million actives.

[9] Average of ten runs.

[0104] The data in Table V demonstrates that the combination of a polyoxyalkylene amine and a Mannich condensation product has a beneficial effect and gives significantly better control of oil screen plugging than the polyoxyalkylene amine component alone.

Claims

1. A fuel additive composition comprising:

(a) a Mannich condensation product of (1) a high molecular weight alkyl-substituted hydroxyaromatic compound wherein the alkyl group has a number average molecular weight of from about 300 to about 5,000 (2) an amine which contains an amino group having at least one active hydrogen atom, and (3) an aldehyde, wherein the respective molar ratio of reactants (1), (2) and (3) is 1:0.1-10:0.1-10; and

(b) a hydrocarbyl-substituted polyoxyalkylene amine having the formula:

$$R\!-\!\left(\!-O-\overset{\displaystyle R_1}{\overset{|}{C}H}-\overset{\displaystyle R_2}{\overset{|}{C}H}-\right)_x\!-A \qquad (I)$$

or a fuel-soluble salt thereof;

wherein R is a hydrocarbyl group having from about 1 to about 30 carbon atoms;

one of R_1 and R_2 is methyl or ethyl and the other is hydrogen, and each R_1 and R_2 is independently

selected in each $-O-CHR_1-CHR_2-$ unit;

A is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms; and

x is an integer from about 5 to about 100;

and wherein the weight ratio of polyoxyalkylene amine to Mannich condensation product is from about 0.5:1 to about 12:1.

2. The fuel additive composition according to Claim 1, wherein the alkyl group on the alkyl-substituted hydroxyaromatic compound has a number average molecular weight of about 400 to about 3,000.

3. The fuel additive composition according to Claim 2, wherein the alkyl group has a number average molecular weight of about 500 to about 2,000.

4. The fuel additive composition according to Claim 3, wherein the alkyl group has a number average molecular weight of about 700 to about 1,500.

5. The fuel additive composition according to Claim 1, wherein the alkyl-substituted hydroxyaromatic compound is a polyalkylphenol.

6. The fuel additive composition according to Claim 6, wherein the polyalkylphenol is polypropylphenol or polyisobutylphenol.

7. The fuel additive composition according to Claim 6, wherein the polyalkylphenol is polyisobutylphenol.

8. The fuel additive composition according to Claim 7, wherein the polyisobutylphenol is derived from polyisobutene containing at least about 70% methylvinylidine isomer.

9. The fuel additive composition according to Claim 1, wherein the amine component of the Mannich condensation product is an alkylene polyamine having the formula:

$$H_2N-(B-NH)_m-H$$

wherein B is a divalent alkylene radical having 1 to about 10 carbon atoms and m is an integer from 1 to about 10.

10. The fuel additive composition according to Claim 9, wherein the alkylene polyamine is polyethylene polyamine.

11. The fuel additive composition according to Claim 10, wherein the polyethylene polyamine is diethylene triamine.

12. The fuel additive composition according to Claim 1, wherein the aldehyde component of the Mannich condensation product is formaldehyde, paraformaldehyde or formalin.

13. The fuel additive composition according to Claim 1, wherein R is an alkyl or alkylphenyl group.

14. The fuel additive composition according to Claim 13, wherein R is an alkylphenyl group.

15. The fuel additive composition according to Claim 1, wherein one of R_1 and R_2 is methyl, and the other is hydrogen.

16. The fuel additive composition according to Claim 1, wherein x is an integer of from about 5 to about 50.

17. The fuel additive composition according to Claim 16, wherein x is an integer of from about 8 to about 30.

18. The fuel additive composition according to Claim 17, wherein x is an integer of from about 10 to about 25.

19. The fuel additive composition according to Claim 1, wherein A is amino, N-alkylamino or a polyamine moiety.

20. The fuel additive composition according to Claim 19, wherein A is amino or N-alkyl amino having from about 1 to about 4 carbon atoms.

21. The fuel additive composition according to Claim 20, wherein A is amino.

22. The fuel additive composition according to Claim 19, wherein A is a polyamine moiety having from about 2 to about 12 amine nitrogen atoms and from about 2 to about 40 carbon atoms.

23. The fuel additive composition according to Claim 22, wherein A is a polyamine moiety derived from a polyalkylene polyamine containing from about 2 to about 12 amine nitrogen atoms and from about 2 to about 24 carbon atoms.

24. The fuel additive composition according to Claim 23, wherein the polyalkylene polyamine has the formula:

$$H_2N\text{-}(R_3\text{-}NH)_z\text{-}H$$

wherein R_3 is an alkylene group having from about 2 to about 6 carbon atoms and z is an integer from about 1 to about 4.

25. The fuel additive composition according to Claim 24, wherein R_3 is an alkylene group having from about 2 to about 4 carbon atoms.

26. The fuel additive composition according to Claim 24, wherein the polyalkylene polyamine is ethylene diamine or diethylene triamine.

27. The fuel additive composition according to Claim 26, wherein the polyalkylene polyamine is ethylene diamine.

28. The fuel additive composition according to Claim 1, wherein the weight ratio of polyoxyalkylene amine to Mannich condensation product is from about 0.5:1 to about 3:1.

29. A fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an amount effective to control engine oil screen plugging of a fuel additive composition as claimed in any preceding claim.

30. The fuel composition according to Claim 29, wherein the composition contains from about 10 to about 2,000 ppm of the Mannich condensation product and from about 10 to about 2,000 ppm of the polyoxyalkylene amine.

31. The fuel composition according to Claim 29, wherein the composition further contains from about 25 to 5,000 ppm by weight of a fuel-soluble, nonvolatile carrier fluid.

32. The fuel composition according to Claim 29, wherein the weight ratio of polyoxyalkylene amine to Mannich condensation product is from about 0.5:1 to about 3:1.

33. A fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of from about 150°F to 400°F and from about 10 to about 70 weight percent of a fuel additive composition as claimed in any one of claims 1 to 28.

34. The fuel concentrate according to Claim 33, wherein the concentrate further contains from about 20 to about 60 weight percent of a fuel-soluble, nonvolatile carrier fluid.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 1299

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,X	US 5 697 988 A (CUNNINGHAM LAWRENCE J ET AL) 16 December 1997 (1997-12-16) * column 5, line 20 - line 33 * ---	1-7, 9-21, 28-34	C10L1/22 C10L1/14 C10L10/00
X	EP 0 811 672 A (ETHYL CORP) 10 December 1997 (1997-12-10) * page 3 * * page 5, line 10 - line 27 * ---	1-8, 12-21, 28-34	
Y	EP 0 569 228 A (ETHYL PETROLEUM ADDITIVES INC) 10 November 1993 (1993-11-10) * page 6, line 24 * * page 9, line 48 - line 56 * ---	1-7, 9-21, 28-34	
D,Y	US 4 231 759 A (UDELHOFEN JOHN H ET AL) 4 November 1980 (1980-11-04) * the whole document * ---	1-7, 9-21, 28-34	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
P,Y	WO 00 61708 A (GUENTHER WOLFGANG ;OPPENLAENDER KNUT (DE); BASF AG (DE); POSSELT D) 19 October 2000 (2000-10-19) * page 8, line 23 * * page 9, line 29 - line 40 * ---	1-10,12, 13, 15-27, 29,31, 33,34	C10L
Y	EP 0 831 141 A (BP CHEMICALS ADDITIVES) 25 March 1998 (1998-03-25) * the whole document * --- -/--	1-10,12, 13, 15-27, 29,31, 33,34	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 July 2001	De La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 1299

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,Y	WO 00 49109 A (CHEVRON CHEM CO) 24 August 2000 (2000-08-24) * page 18, line 24 - line 29 *	1-7,9-34	
D,Y	EP 0 647 700 A (ETHYL CORP) 12 April 1995 (1995-04-12) * page 4 - page 5 * * page 8, line 14 - line 17 *	1-7,9-34	
D,A	US 5 514 190 A (CUNNINGHAM LAWRENCE J ET AL) 7 May 1996 (1996-05-07) * column 8, line 15 - line 33 *	1-34	
D,A	EP 0 356 725 A (BASF AG) 7 March 1990 (1990-03-07) * the whole document *	1,13-21	
D,A	EP 0 781 793 A (CHEVRON CHEM CO) 2 July 1997 (1997-07-02) * claims 6,7; example 1 *	1,13-19, 22-27	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	WO 97 43359 A (CHEVRON CHEM CO) 20 November 1997 (1997-11-20) * claims 1,21-23,33-36,53-55,57,58,76-78; example 11 *	1,13-21, 29-34	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 July 2001	De La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 30 1299

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-07-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5697988 A	16-12-1997	AU 678514 B	29-05-1997
		AU 7445294 A	27-04-1995
		CA 2133796 A	07-04-1995
		DE 69421784 D	30-12-1999
		DE 69421784 T	18-05-2000
		EP 0647700 A	12-04-1995
		JP 2744205 B	28-04-1998
		JP 7197052 A	01-08-1995
		GB 2261441 A,B	19-05-1993
EP 0811672 A	10-12-1997	US 5634951 A	03-06-1997
		AU 728980 B	25-01-2001
		AU 2473097 A	11-12-1997
		JP 10060460 A	03-03-1998
		SG 50843 A	20-07-1998
		US 5725612 A	10-03-1998
EP 0569228 A	10-11-1993	AU 3833793 A	11-11-1993
		CA 2095683 A	07-11-1993
		DE 69319275 D	30-07-1998
		DE 69319275 T	12-11-1998
		JP 7268365 A	17-10-1995
		US 5551957 A	03-09-1996
		US 5679116 A	21-10-1997
US 4231759 A	04-11-1980	NONE	
WO 0061708 A	19-10-2000	DE 19916512 A	19-10-2000
		AU 4745700 A	14-11-2000
EP 0831141 A	25-03-1998	JP 10158323 A	16-06-1998
		US 5876468 A	02-03-1999
WO 0049109 A	24-08-2000	US 6217624 B	17-04-2001
		AU 3233200 A	04-09-2000
		BR 0004867 A	19-12-2000
		CN 1296520 T	23-05-2001
		EP 1080166 A	07-03-2001
EP 0647700 A	12-04-1995	AU 678514 B	29-05-1997
		AU 7445294 A	27-04-1995
		CA 2133796 A	07-04-1995
		DE 69421784 D	30-12-1999
		DE 69421784 T	18-05-2000
		JP 2744205 B	28-04-1998
		JP 7197052 A	01-08-1995

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 30 1299

This annex lists the patent family membersrelating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-07-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0647700 A		US 5697988 A	16-12-1997
US 5514190 A	07-05-1996	NONE	
EP 0356725 A	07-03-1990	DE 3826608 A	08-02-1990
		CA 1338968 A	04-03-1997
		DE 58908792 D	02-02-1995
		DK 383089 A	06-02-1990
		ES 2065953 T	01-03-1995
		US 5112364 A	12-05-1992
EP 0781793 A	02-07-1997	CA 2191919 A	20-06-1997
		DE 69608401 D	21-06-2000
		DE 69608401 T	11-01-2001
		DE 69612724 D	13-06-2001
		EP 0781794 A	02-07-1997
		JP 9221545 A	26-08-1997
WO 9743359 A	20-11-1997	US 5669939 A	23-09-1997
		US 5851242 A	22-12-1998
		AU 714825 B	13-01-2000
		AU 3002397 A	05-12-1997
		AU 715037 B	13-01-2000
		AU 3063597 A	05-12-1997
		BR 9702216 A	28-12-1999
		BR 9702218 A	28-12-1999
		CA 2226672 A	20-11-1997
		CA 2226982 A	20-11-1997
		CN 1193338 A	16-09-1998
		CN 1193339 A	16-09-1998
		EP 0840774 A	13-05-1998
		EP 0845023 A	03-06-1998
		JP 11509890 T	31-08-1999
		JP 11509559 T	24-08-1999
		NZ 329354 A	28-10-1999
		NZ 329355 A	28-10-1999
		WO 9743360 A	20-11-1997

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82